

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
6 May 2004 (06.05.2004)

PCT

(10) International Publication Number
WO 2004/037509 A1

(51) International Patent Classification⁷: **B29C 43/02**,
F16J 15/14

(21) International Application Number:
PCT/US2003/031190

(22) International Filing Date: 1 October 2003 (01.10.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2002-310007 24 October 2002 (24.10.2002) JP

(71) Applicant (for all designated States except US): 3M IN-
NOVATIVE PROPERTIES COMPANY [US/US]; 3M
Center, Post Office Box 33427, Saint Paul, MN 55133-
3427 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): KITANO, Shuichi
[JP/JP]; 5-4-7-202 Chuou, Sagami-hara-city, Kanagawa
229-0039 (JP).

(74) Agents: KNECHT, Harold C., III, et al.; Office of In-
tellectual Property Counsel, Post Office Box 33427, Saint
Paul, MN 55133-3427 (US).

(81) Designated States (national): AE, AG, AL, AM, AT (util-
ity model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA,
CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (util-
ity model), DE, DK (utility model), DK, DM, DZ, EC, EE
(utility model), EE, EG, ES, FI (utility model), FI, GB, GD,
GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN,
MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU,
SC, SD, SE, SG, SK (utility model), SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

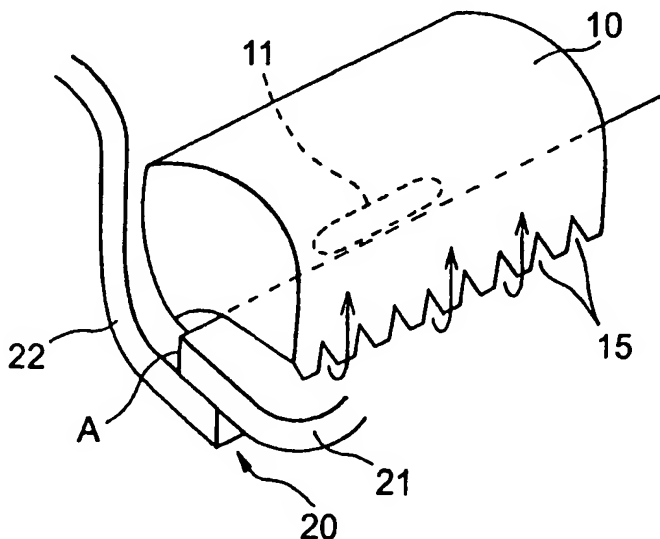
(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: SEALING MATERIAL



(57) Abstract: A sealing material for
sealing a joint portion (10) that can prevent
the trapping of air bubbles (51) and does
not give rise to poor appearance or defects in
paint film even if the joint portion (10) has an
irregular surface shape. The sealing material
comprises a shaped body (10) of heat-curable
resin composition which is capable of
melting-hardening, has sufficient width and
length to substantially cover a discontinuous
joint portion (21, 22), and which is provided
with a plurality of communicating grooves
(15) on the surface to be brought into
contact with the joint portion (21, 22). The
communicating grooves (15) connect one
side of the shaped body (10) and the other
opposing side of the shaped body (10).

Sealing Material

Field of the Invention

5 The present invention relates to a sealing material, in particular, to a melting-hardening type or melt flowable type sealing material used for sealing a discontinuous joint portion, for example, a lap joint, step, joint, welded portion, etc., and more particularly, to such a sealing material for use in vehicles such as an automobile.

Background of the Invention

10 A discontinuous joint portion formed, for example, by superimposing steel plates is found in a vehicle such as, for example, a car or a truck. Discontinuous joint portions are formed for various purposes in vehicles, as can be typically seen in a roof ditch of an automobile. A roof ditch of an automobile is formed in longitudinal direction by folding and superimposing side edges of a roof panel and a side panel to each other. This roof
15 ditch has a U-shaped groove for collecting water etc. therein and discharging them out of the vehicle.

A discontinuous joint is usually sealed with a sealing material in order to prevent ingress of water, dust, etc., to avoid leakage of water, or to improve appearance of a joint or the effect of painting. A sealing material may be used in liquid state or in solid state
20 depending upon the requirements of execution of work. For execution of work of above-mentioned roof ditch, a plastisol in liquid or paste form consisting of a plasticizer and polyvinyl chloride (PVC) particles dispersed therein has been employed. However, this sealing material may produce dioxin, a chloride that is highly toxic and is hard to be decomposed, when it is burnt, and in addition, a phthalate type plasticizer which is a
25 suspected environmental hormone is often used. Japanese Unexamined Patent Publication (Kokai) No. 2001-115142 (Paragraphs 0005 to 0009) discloses an alternative sealing material having a composition containing a curable resin such as urethane resin, silicone resin, etc., and hardened particles of the sealing material.

30 Joint portions in vehicles can include irregular surfaces (steps, spots, marks of laser welding, etc., deformations, and the like), and hence, if sealing material is a liquid or paste, one often encounters difficulties in the execution of work. Therefore, use of sealing material having a definite shape such as a sheet or a tape has been proposed. For example,

Japanese Unexamined Utility Model Publication (Kokai) No. 61-176232 (Fig. 1) discloses a sealer tape in the form of a tape for sealing a steel plate joint found in a car body or the like, wherein bead portion is formed as minute ruggedness in the tape surface adhered to the steel plate, characterized in that plane portions extending in parallel to the steel plate are provided on both sides of the bead portion in longitudinal direction of the tape. This sealer tape, however, is only intended to be brought into close contact with the joint portion of the steel plate. Thus, although some effect can be expected on the prevention of separation of both ends, there is still room for improvement in one or more of the complete and close contact with the joint portion as well as in stable sustenance of this contact, in the painting efficiency of the sealer tape, in the ability of seal to follow-up irregular surface shape of the joint, and the like.

Japanese National Publication (Kohyo) No. 09-505335 (Claims 1 to 22, Figs. 1a and 1b) discloses replacing the solid sealing material by a form capable of melting-flowing, that is, a form in which the sealing material can be heated and fluidized after execution of work, and after it is thus brought into completely close contact with the joint portion, it can be hardened again. This sealing material comprises at least one layer essentially consisting of one or more polymer which is semi-crystalline at room temperature and thermoplastic, and which is capable of melting-flowing, and one or more filler that is substantially non-reactive as required.

Sealing material that is capable of melting-flowing is useful in forming a seal which can be painted in the production line of a vehicle such as an automobile. With this type of sealing material, however, there is still problems left to be solved, that is, problems such as poor appearance due to trapped air bubbles, or occurrence of defects in a paint film formed on the seal.

Figs. 1A through 1E are views showing sequentially the occurrence of problems due to trapping of air bubbles in a roof ditch of an automobile as an example. A roof ditch is formed by folding two steel sheet panels 21 and 22, and superimposing and joining the portions thereof so as to form U-shaped groove for collecting water etc., and discharging it out of the vehicle. A sealing material 50 that is capable of melting-flowing is filled into the groove to form a seal for prevention of rusting and improvement of appearance, and the seal can be painted (not shown) to further improve the appearance and quality of the seal.

First, as shown in Fig. 1A, a strip-shaped sealing material 50 capable of melting-flowing is mounted to U-shaped groove of a roof ditch so as to cover the discontinuous joint (step) A on the bottom.

Next, as shown in Fig. 1B, the sealing material 50 is heated to start melting. The sealing material 50 begins to melt at the interface in contact with the panel, and begins to flow before it fills the step A completely. As heating is continued, as shown in Fig. 1C, a major portion of the groove is filled by the melt sealing material 50. Even if heating is performed carefully, a small bubble (air) 51 is inevitably trapped in the melt in this process. Trapping of air bubbles takes place markedly, especially when there is a step difference of panels as shown in the Figure, spots, marks of laser welding, deformation of panels, etc.

The air bubble 51 trapped in the sealing material 50 may be acceptable if it remains inside the seal (hardened seal) as it is. However, as shown in Fig. 1D, it gradually rises and emerges on the surface since the viscosity of the melted sealing material 50 is low. If the rising air bubble 51 reaches the surface of the melted sealing material 50, as shown in Fig. 1E, it is left as a depression, pinhole, crater etc. on the surface, leading to a defect in appearance when the sealing material 50 is hardened to form a seal. When such a surface defect is present, painting on the seal may not conceal the defect, and the paint may not be adhered to the surface satisfactorily.

Therefore, there is a need for a sealing material, like that used for sealing discontinuous joint portion of a vehicle, which exhibits one or more of being easy to be handled, does not generate harmful gas to environment, and which can prevent trapping of air bubbles even when the surface of the joint portion is of irregular shape, and therefore does not give rise to poor appearance or painting defects.

Summary of the Invention

According to the present invention, the above need can be met by providing a sealing material, like that used for sealing discontinuous joint portion of a vehicle, comprising a shaped body of a heat-curable resin composition, which is capable of melting-hardening and which has sufficient width and length to substantially cover the joint portion. The shaped body is provided with a plurality of communicating grooves, and each of the communicating grooves has the starting end on one side of the shaped

body and a terminating end on the other opposing side of the shaped body. The grooves can be aligned in a predetermined direction and arranged in parallel to each other on the surface of the shaped body to be brought in contact with the joint portion.

The joint portion can be, for example, a lap joint of longer sides of longitudinal metal plates. The joint portion can also define a bottom surface of a groove of a longitudinal grooved plate. The grooved plate can be, for example, a roof ditch of an automobile. The communicating groove can have a cross-sectional shape such as, for example, a rectangle, semicircle, V-shape, U-shape, and trapezoid.

The heat-curable resin composition can comprise a heat-curable epoxy-containing material; a thermoplastic polyamide component having softening point lower than the curing temperature of the epoxy-containing material; and a curing agent for the epoxy-containing material. Alternatively, the heat-curable resin composition can comprise an epoxy-containing material comprising a hygroscopic epoxidized thermoplastic resin; a curing agent for the epoxy-containing material; a filler; and an optional plasticizer. The hygroscopic epoxidized thermoplastic resin can be at least one of an epoxidized ethylene thermoplastic resin and an epoxidized styrene thermoplastic resin.

Brief Description of Drawings

Figs. 1A – 1E are sectional views useful for explaining occurrence of an air bubble in conventional melting-flowing type sealing material.

Fig. 2 is a perspective view showing a sealing material for vehicle according to a preferred embodiment of the present invention.

Fig. 3 is a perspective view showing application of the sealing material shown in Fig. 2 to a roof ditch.

Fig. 4 is a perspective view showing the principle of the prevention of air bubble trapping in the roof ditch shown in Fig. 3.

Fig. 5 is a sectional view schematically showing an escape path of an air bubble in the roof ditch shown in Fig. 3.

Fig. 6 is a sectional view schematically showing an escape path of an air bubble in the roof ditch shown in Fig. 3.

Fig. 7 is a bottom view showing the arrangement of the communicating grooves in the sealing material shown in Fig. 2.

Fig. 8 is a longitudinal sectional view showing the shape of the communicating grooves of the sealing material shown in Fig. 2.

Figs. 9A and 9B are bottom views showing another arrangement pattern of the communicating grooves in the sealing material of the present invention.

5 Fig. 10 is a bottom view showing the arrangement pattern of communicating grooves in a sealing material used in a comparative example.

Detailed Description

10 A sealing material according to the present invention can be advantageously implemented in various forms. The sealing material of the present invention will be described below with special reference to its usage for a vehicle and, in particular, in a roof ditch of an automobile. It is to be understood that the invention is by no means limited to this application example.

15 The sealing material of the present invention is intended to seal a discontinuous joint portion of an article, that is, to form a seal on the article, especially a vehicle. As used herein, "article" means typically a vehicle in a broader sense, such as a car, truck, electric train, ship, aircraft, etc. and may include a structure such as a building, bridge, etc., as required. As used herein, "discontinuous joint portion" means a joint portion having any irregular surface shape, such as a lap joint, step, joint, welded joint, etc., and
20 may include step difference where no joint processing has been actually performed.

In the practice of the present invention, an irregular joint portion is preferably a lap joint of two long steel plates with the longer sides being overlapped and joined to each other. More preferably, the joint portion defines the bottom of grooves of long grooved steel plates. Such a grooved steel plate is typically found in a roof ditch of a car.

25 The sealing material of the present invention is usually a solid, and is provided in shaped form, that is, as a shaped body. The form of the shaped body may vary widely depending upon the intended use of the sealing material, and typically includes a rope, tape, ribbon, sheet, etc. These shaped bodies may be cut into a strip of a predetermined length, or long shaped body may be wound in a roll and may be cut into a required length
30 for each application.

The sealing material of the present invention comprises a heat-curable resin composition, and is capable of melting-hardening. That is, the sealing material is solid at

ordinary temperature, and melts into fluidized state when heated to a predetermined temperature. The sealing material in fluidized state is hardened (cured) by subsequent cooling, and does not melt again.

5 More specifically, the heat-curable resin composition which forms the sealing material of the present invention is considered to be capable of melting-flowing. That is, when the sealing material containing this resin composition that covers the discontinuous joint portion of an article is heated, it comes into close contact with the surface of the discontinuous joint portion, thereby expelling trapped air outwards. During the heating cycle, the resin composition is heated and acquires tackiness, and is adhered to the surface
10 of the article. Since this sealant composition is heat-curable, it is hardened by application of heat (for example, by cross-linking through covalent bond), and does not flow again by subsequent cooling and reheating.

The heat-curable resin composition of the present invention, once hardened, preferably exhibits excellent flexibility at low temperature and can be bent easily around a
15 mandrel without producing a crack or fracture. Preferably, but without limitation, the hardened resin composition exhibits, when tested at a temperature of -20 °C, elongation percentage of at least 10%. Basically, the hardened resin composition exhibits, when tested at a temperature of -20 °C, elongation percentage of at least 2%. In such a case, a paint used for vehicle, especially a car paint, exhibits an elongation percentage that is
20 approximately same as or smaller than the hardened resin composition, when tested at a temperature of -20 °C. As a result, even if above-mentioned paint is coated on the exposed surface of the hardened resin composition, the hardened resin composition can be prevented from producing a crack or fracture prior to the paint. Thus, the sealing material of the invention can sustain tight covering of a discontinuous joint portion, and avoid
25 ingress of moisture, dust, snow or other undesirable component into the joint portion. Composition and the like of the heat-curable resin composition will be described in detail after the form etc. of the sealing material of the present invention is described below.

The sealing material of the present invention especially has characteristic features in its form. Thus, the sealing material is characterized in that:

30 (1) it has sufficient width and length to substantially cover the discontinuous joint portion of an article intended for the sealing material to be applied;

(2) a plurality of communicating grooves aligned in a predetermined direction in parallel to each other are provided on the surface of the sealing material to be brought into contact with the joint portion of an article;

5 (3) each of the communicating grooves has a starting end at one side of the sealing material and a terminating end at the other opposing end of the sealing material.

These features will be described below with reference to Fig. 2 showing a sealing material for a roof ditch that is a typical example of the present invention.

10 Fig. 2 is a perspective view showing a sealing material for vehicle according to a preferred embodiment of the present invention. The sealing material 10 is in the form of a strip having sufficient width and length to cover the discontinuous joint portion of the roof ditch after melting-hardening. Dimensions of the sealing material may vary widely in accordance with the intended use and the form of provision of the sealing material, and in the case of strip form as shown in the figure, are typically about 50 to 3,000 mm in length, about 3 to 50 mm in width, and about 1 to 10 mm in thickness.

15 The sealing material 10 has a multiplicity of regularly arranged communicating grooves 15 on one of its major surfaces (the surface to be brought into contact with the roof ditch). The communicating grooves 15 are arranged, as shown in Fig. 7, in parallel to and spaced apart from each other at a pitch p between ridges, and each of the communicating grooves 15 is aligned in a predetermined direction. In the illustrated
20 example, respective communicating grooves are aligned at an angle θ_1 to the longitudinal direction. Thus, in this example, the angle θ_1 is equal to 90 degrees so that respective communicating grooves 15 are perpendicular to the sealing material 10. Each of the communicating grooves 15 has a starting end on one side of the sealing material 10 and a terminating end on the other opposing side of the sealing material 10, so that air bubbles
25 trapped between the sealing material 10 and the roof ditch during execution of work do not remain trapped, but can be discharged outwards. Although the communicating grooves 15 are continuously arranged in the illustrated example, they may be spaced apart from each other, as required, since execution of work becomes easier in this construction which increases the surface area in contact with the roof ditch.

30 In the illustrated sealing material 10, each of the communicating grooves 15 has a V-shaped cross section (cross section in the form of a saw tooth), as shown in Fig. 8, with the apex angle θ_2 of about 80 degrees. The apex angle θ_2 , and aforementioned pitch p and

alignment angle θ_1 may be respectively varied arbitrarily, depending upon desired effect of the sealing material 10. For example, the alignment angle θ_1 is typically in the range of 20 to 90 degrees, and preferably may be varied arbitrarily within the range. More specifically, the sealing material is as shown in Fig. 9A if alignment angle θ_1 is 60
5 degrees, and as shown in Fig. 9B if alignment angle θ_1 is 30 degrees. The apex angle θ_2 is typically in the range of 30 to 150 degrees, and preferably in the range of 60 to 120 degrees. The pitch p is typically in the range of 0.1 to 4 mm, and preferably in the range of 0.3 to 2.1 mm.

Although communicating grooves 15 having V-shaped cross section are shown in
10 Fig. 8, shape of the communicating groove is not limited to this example. For example, the communicating groove may be rectangle, semicircle, U-shape, or trapezoid in cross section. Two or more cross-sectional shapes may be combined arbitrarily as required.

Although a sealing material having regularly arranged communicating grooves in a definite direction is shown in the figures, the communicating groove may be arranged in
15 other pattern. For example, the sealing material may be constructed such that a second group of communicating grooves consisting of a plurality of communicating groove aligned in a predetermined direction in parallel to each other crosses the above-described group of communicating grooves. Thus, by providing two groups of communicating
20 grooves orthogonal to each other so as to form communicating grooves in the form of a lattice, discharge of air bubbles can be promoted.

Fig. 3 is a perspective view showing a roof ditch of a car to which the sealing material 10 shown in Fig. 2 can be applied. A roof ditch 20 is fabricated by processing two panels, roof panel 21 and side panel 22, respectively in right angle, and is provided with a U-shaped ditch as a flowing path for rain water or the like. By sealing the step A
25 formed by a lap joint of the two panels with the sealing material 10, trapping of air bubbles and hence production of painting defects can be prevented as has been described before with reference to Fig. 1. Also, ingress of moisture, dust, or other undesirable component in the lap joint portion and corrosion caused by such an ingress can be prevented.

30 It will be easily understood from Figs. 4 to 6 that trapping of air bubbles can be prevented by using the sealing material of the present invention.

For example, as shown in Fig. 4, when there is a fear of a large bubble of air 11 being trapped as it is at the step A of the lap joint of a roof panel 21 and a side panel 22, it is impossible for a conventional sealing material to expel the air bubble. On the other hand, in accordance with the present invention, a group of communicating grooves are provided on the lower surface of the sealing material 10 so that the air bubble can be expelled from the side of the roof panel 21 as shown by the arrow. That is, as shown in Fig. 5, the air bubble 11 is discharged along the wall surface of the roof panel 21 outwards through unclosed communicating groove (not shown). Even if the wall surface of the roof panel 21 is closed by the sealing material 10, the air bubble 11 left on the roof panel 21 can escape along the side panel 22.

In the sealing material of the present invention, any resin composition may be used as the heat-curable resin composition as long as it exhibits above-described behavior of solid - melting - flowing - solidifying, and it does not adversely affect the operative effect of the present invention. Suitable heat-curable resin composition is typically a resin composition containing epoxy-containing material as a main constituent.

Suitable heat-curable resin composition for implementation of the present invention is, for example, a resin composition which comprises:

- a heat-curable epoxy-containing material;
- a thermoplastic polyamide component having softening point not higher than the curing temperature of said epoxy-containing material; and
- a curing agent of said epoxy-containing material.

More specifically, in the above-described heat-curable resin composition, the epoxy-containing material contributes to the ultimate strength and heat resistance of the resin composition, while the thermoplastic polyamide component contributes to the shape-follow up characteristic and flexibility, especially at low temperature. The curing agent enables hardening of the resin composition. Preferably, the curing agent is activated thermally and acts such that the resin composition is hardened by exposure to a suitable heat source in a suitable time.

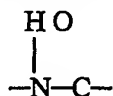
Useful epoxy-containing material is an epoxy resin having at least one oxirane ring polymerizable by ring opening reaction. Such materials are known as epoxide in broader sense, and include both monomer and polymer epoxide, and are present as aliphatic, alicyclic and aromatic compounds. Such materials generally contain, in average, at least

two epoxy groups, preferably two or more epoxy groups, per molecule. Such materials are called specifically as polyepoxide, having epoxy functionality slightly less than 2.0, and include, for example, epoxy-containing material of 1.8 in epoxy functionality. "Average" number of epoxy groups per molecule is defined as the number of epoxy groups in an epoxy-containing material divided by the total number of epoxy molecules. Polymer epoxide includes linear polymer having epoxy group at the ends (for example, polyalkylene glycol diglycidyl ether), polymer having backbone oxirane units (for example, polybutadiene polyepoxide), and polymer having epoxy group as side chain (for example, glycidyl methacrylate polymer or copolymer). Molecular weight of the epoxy-containing material may vary in the range of 58 to about 100,000 or higher. Mixture of various epoxy-containing materials may be used.

Useful epoxy-containing materials include materials containing epoxy cyclohexane carboxylate as represented by 3,4-epoxy cyclohexylmethyl-3,4-epoxy cyclohexane carboxylate, 3,4-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methyl cyclohexane carboxylate, and bis (3,4-epoxy-6-methyl cyclohexylmethyl) adipic acid ester. Particularly useful epoxy-containing material is diglycidyl ether monomers such as glycidyl ether of polyhydric phenol (for example, diglycidyl ether of 2,2-bis-(2,3-epoxypropoxyphenol) propane) obtained by reaction of polyhydric phenol in excess with chlorohydrin such as epichlorohydrin.

Many epoxy-containing material is commercially available, and can be used for implementing the present invention, for example, under the trade name of EPIKOTE 1001, EPIKOTE 1002, EPIKOTE 1003, EPIKOTE 1004, EPIKOTE 828, or EPIKOTE 154, available from Yuka Shell Epoxy Co.

A thermoplastic polyamide component is also contained in the heat-curable resin composition of the present invention. This thermoplastic polyamide component refers to polymer material containing amide group represented by following general formula:



and such a material exhibits thermoplastic processing characteristics. That is, this material is softened by heating, can be shaped by flowing, and is hardened by cooling. Further, this material can be softened again by reheating. The thermoplastic polyamide component can achieve desirable mixing not only with the epoxy-containing material, but also with other

component of the resin composition which does not promote hardening of the epoxy-containing material. The thermoplastic polyamide component also contributes to excellent low temperature characteristics, especially to its flexibility, of the sealant composition.

Desirable thermoplastic polyamide component is mixed in melt phase (that is, melt-mixed) with the epoxy-containing material, and preferably forms a uniform mixture of single phase when it does not harden the epoxy-containing material. Formation of a uniform single phase is evident from transparency of such a mixture (melt-mixture). Preferably, for 100 parts by weight of aforementioned epoxy-containing material, about 90 to about 350 parts by weight of polyamide component is contained. If the content of polyamide component is about 90 parts by weight or less, the hardened resin composition tends to become brittle. On the other hand, if the content of polyamide component is about 350 parts by weight or more, the hardened resin composition is not sufficiently cross-linked and tends to be easily fluidized upon reheating. Consequently, when the epoxy-containing material is hardened, composition of multiple phases or separate phases may be produced. One phase is produced from hardened epoxy-containing material, and the other phase is produced as a result of thermoplastic polyamide component. But, since both phases are produced from a uniform single phase consisting of the epoxy-containing material and the thermoplastic polyamide component, both phases are not distributed unevenly even when the epoxy-containing material is hardened. Therefore, the resin composition is given both characteristics attributable to the epoxy-containing material and the thermoplastic polyamide component. To the extent that desirable characteristics are given to the resin composition by the blended thermoplastic polyamide component, unevenness of distribution is acceptable.

Desirable thermoplastic polyamide component has a softening point not higher than the curing temperature of the epoxy-containing material in order to prevent the epoxy-containing material from being hardened when the resin composition is heated to form a seal on the desired surface. Thus, the resin composition melts by heating, and can easily penetrate into discontinuous portion. When the resin composition is used in automobile industry, the thermoplastic polyamide component has typically a softening point not higher than 180 °C.

The resin composition further comprises a curing agent for hardening the epoxy-containing material. Preferably, the curing agent is activated thermally to induce

hardening of the epoxy-containing material under the influence of heat. For example, useful curing agents that can be activated thermally include amide group containing amine or imidazole. Preferably, dicyandiamide is representative as a curing agent containing amide group. Triazine derivative is representative as a curing agent containing imidazole.

5 A curing agent containing dicyandiamide is commercially available, for example, under the trade name of "EH3636" from ACR Co. A curing agent containing triazine derivative is commercially available under trade name of "2MZA" from Shikoku Kasei Co.

The resin composition further may contain, as required, various additives such as a filler consisting of calcium carbonate or silica powder, for example, an antioxidant
10 commercially available under trade name of "Irganox 1010" from Chiba Geigy Co., for example, a ultraviolet absorbing agent commercially available under trade name of TINUVINTM P from Chiba Geigy Co., for example, or surfactant commercially available under trade name of "FC36" from 3M Co.

The heat-curable resin composition is solid at room temperature. It is desirable
15 that the resin composition has some tackiness at or slightly below room temperature. Such tackiness permits members including the resin composition to be positioned first, when covering joints or seams, for example, in the roof ditch of a vehicle. When the resin composition is in the form of a rope, tape, strip or similar shape, it permits quick mounting, and can eliminate the need of skillful and laborious processing of the material
20 after execution of work (for example, giving acceptable appearance to the applied sealing material).

Another preferable heat-curable resin composition for implementation of the present invention is a resin composition comprising, for example:

an epoxy-containing material containing low hygroscopic epoxy thermoplastic
25 resin;
a curing agent for said epoxy-containing material; and
a filler.

More specifically, the epoxy-containing material used as a first component in the heat-curable resin composition contains a low hygroscopic epoxidized thermoplastic resin,
30 and further contains an epoxy resin and, as required, a cosolubilizing agent.

(1) Low hygroscopic epoxidized thermoplastic resin

An epoxidized thermoplastic resin is a thermoplastic resin having an epoxy group. In general, a thermoplastic resin can give a definite shape to the heat-curable resin composition. An epoxidized thermoplastic resin contributes to heat curing reaction by the presence of the epoxy group. As a result, when the heat-curable resin composition is hardened, the hardened product acquires heat resistance and durability. In the sealer application for a roof ditch of an automobile, the presence of the epoxy group improves the close contact between the hardened product and an automobile paint (for example, organic solvent-based acryl paint or organic solvent-based alkyd paint) and cation electrodeposition-coated car steel plate. Since the sealer is mounted to car body before car painting process, painting can be performed on the sealer during the painting of car body so as to give it the same color as the car body. As a result, covering material such as a molding is not required, and artistic appearance of the car body is improved. Close contact with the steel plate also improves durability and tightness of the sealer.

In the heat-curable resin composition, it is required that the hygroscopicity of the epoxidized thermoplastic resin is as low as possible, since absorption of moisture by the heat-curable resin composition is prevented by this low hygroscopicity, and consequently the low hygroscopicity offers great advantage for subsequent car painting process. Also, storage or other handling of the heat-curable resin composition is very much simplified. As used herein, "low hygroscopicity" means that the epoxidized thermoplastic resin has saturation water absorption ratio of 0.2 wt% or less at 35 °C and relative humidity of 80% RH. Such an epoxidized thermoplastic resin has solubility parameter (SP) of typically about 9 or less. As used herein, the solubility parameter is that defined by Small's equation (as described in, A. Small, J. Appl. Chem. 3, 71 (1953)).

Usually, in view of flow characteristics during shaping process and heat melting, such an epoxidized thermoplastic resin has molecular weight of 1,000 to 10,000. In view of heat resistance, durability, and close contact with paint film and water-absorbing ratio, the epoxidized thermoplastic resin generally has epoxy equivalent of 200 to 15,000.

A typical example of above-described epoxidized thermoplastic resin is an epoxidized ethylene thermoplastic resin. This resin exhibits low hygroscopicity due to the presence of the ethylene portion. The epoxidized ethylene thermoplastic resin is preferably an ethylene-glycidyl (meth)acrylate copolymer. As has been disclosed as a

component of an adhesive and hot-melt composition in Japanese Unexamined Patent Publication (Kokai) Nos. 9-137028 and 10-316955, the ethylene-glycidyl (meth)acrylate copolymer is epoxidation of polyethylene, and is obtained usually by copolymerization of ethylene and glycidyl methacrylate. As a result, the ethylene-glycidyl (meth)acrylate
5 copolymer is composed of ethylene portion and glycidyl (meth)acrylate portion. In this case, the ethylene portion contributes to the low hygroscopicity of the heat-curable resin composition, and the glycidyl (meth)acrylate portion contributes to the close contact with the car paints and cation electrodeposition-painted car steel plate to be described later.

The ethylene-glycidyl (meth)acrylate copolymer is preferably composed with the
10 monomer weight ratio of ethylene and glycidyl (meth)acrylate in the range of 50 : 50 to 99 : 1. The ethylene-glycidyl (meth)acrylate copolymer containing ethylene exceeding the upper limit tends to encounter difficulty in giving desired mechanical strength and durability to the hardened product. On the other hand, the ethylene-glycidyl (meth)acrylate copolymer containing ethylene less than the lower limit tends to be unable
15 to provide desired low hygroscopicity to the hardened product.

Typical ethylene-glycidyl (meth)acrylate copolymer melts easily at relatively low temperature of about 120 °C or lower, and when the heat-curable resin composition containing such a copolymer is heated and fluidized to seal a joint portion, high fluidity can be obtained, and as a result, uniform and smooth appearance of the seal can be
20 obtained. Also, during heating-mixing process in the preparation of the sealer, kneading can be performed at relatively low temperature so that there is little fear of the reaction of a heat-curable component and a curing agent taking place in the kneading process, and hence a curing agent with higher reactivity can be chosen.

A ternary ethylene-glycidyl (meth)acrylate copolymer which has a third
25 component other than ethylene and glycidyl (meth)acrylate copolymerized or graft copolymerized may be used as the epoxidized thermoplastic resin as long as the effect of the present invention is not impaired. An example of such a ternary copolymer is obtained by copolymerization of alkyl (meth)acrylate or vinyl acetate, and as a graft polymer, by graft polymerization of polystyrene, polyalkyl (meth)acrylate and acrylnitrile-styrene
30 copolymer.

Another typical example of the epoxidized thermoplastic resin is an epoxidized styrene thermoplastic resin, which exhibits low hygroscopicity due to the presence of

conjugate diene. The epoxidized styrene thermoplastic resin is a block copolymer having a hard segment consisting of polystyrene and a soft segment consisting of epoxidized polybutadiene and giving rubber-like elasticity to the elastomer. Epoxidized polyisoprenemay be used in place of, or in conjunction with, epoxidized polybutadiene.

5 Usually, the glass transition temperature (T_g) of an epoxidized styrene thermoplastic resin is very low, and is -70 to -50 $^{\circ}\text{C}$, and durability (especially vibration durability) at low temperature as low as -30 $^{\circ}\text{C}$ of hardened product of the heat-curable resin composition can be thereby improved. Consequently, the epoxidized styrene thermoplastic resin can be advantageously used for sealer application of the portion
10 subjected to repeated stress at low temperature, for example, for above-described sealer application of the roof ditch of a car. In the sealer application of the roof ditch of a car, due to the presence of styrene portion and epoxy group of the epoxidized styrene thermoplastic resin, the hardened product comes into close contact with a car paint (for example, organic solvent acryl paint or organic solvent alkyd paint) and cation
15 electrodeposition-painted car steel plate.

 Examples of such a epoxidized styrene thermoplastic resin are styrene-epoxidized butadiene-styrene copolymer and styrene -epoxidized isoprene-styrene copolymer. In either case, epoxidization is performed by epoxidization of unsaturated bond of conjugate diene.

20 The low hygroscopic epoxidized thermoplastic resin is preferably contained in the heat-curable resin composition in an amount of 10 to 90 wt%. If the content is less than about 10 wt%, heat resistance and low hygroscopicity are insufficient, and if the content is more than about 90 wt%, relative amount of the filler is reduced and sufficiently low coefficient of linear expansion cannot be obtained.

25 (2) Epoxy resin

 Epoxy-containing material includes, in addition to above-described epoxidized thermoplastic resin, liquid and solid epoxy resin such as bisphenol A epoxy resin, bisphenol F epoxy resin, novolac epoxy resin, glycidyl amine epoxy resin, to improve heat resistance and durability of hardened product of the heat-curable resin composition and
30 close contact with above mentioned car paint. Desirable epoxy resins are epoxy resins having relatively low polarity such as hydrated bisphenol A epoxy resin, alicyclic epoxy resin, linear aliphatic epoxy resin such as butadiene backbone epoxy resin, or glycidyl

ester epoxy resin such as dimer acid modified epoxy resin, since these epoxy resins have excellent compatibility to low hygroscopic component such as ethylene portion and butadiene portion included in said epoxidized thermoplastic resin. In addition, water absorption by hardened product is prevented, which is advantageous for car painting process as has been described. Amount of this epoxy resin is typically 0 to 500 parts by weight, preferably 5 to 400 parts by weight, for 100 parts by weight of component (1), that is, low hygroscopic epoxidized thermoplastic resin.

(3) Compatibilizing agent

Compatibilizing agent may be further contained, as required, in the epoxy-containing material. For 100 parts by weight of the low hygroscopic epoxidized thermoplastic resin, typically 0 to 300 parts by weight, and preferably 1 to 100 parts by weight of the compatibilizing agent may be contained, so as to increase compatibility of low hygroscopic epoxidized thermoplastic resin and epoxy resins. As long as above-mentioned compatibility is achieved, there is no special limitation to the compatibilizing agent. Preferably, the compatibilizing agent comprises polyester resin or ethylene vinyl acetate copolymer (EVA). In particular, when polyester resin is blended with low hygroscopic epoxidized thermoplastic resin in a specified ratio, it prevents separation of the low hygroscopic epoxidized thermoplastic resin and epoxy resin, and in addition, greatly improve fluidity at the curing temperature (100 to 160 °C) of the heat-curable resin composition.

In combination with above-described epoxy-containing material, a curing agent for this material is used. The curing agent hardens epoxy group contained in the epoxidized thermoplastic resin and the epoxy resin and provide cross-linking structure in the heat-curable resin composition to produce a hardened product.

In accordance with the present invention, there is no limitation to the curing agent as long as a hardened product can be obtained. Therefore, the curing agent may include amine compounds such as dicyandiamide, acryl compounds having carboxyl group (including acid anhydride) in the molecule or rosin, imidazole derivatives, BF₃ complexes, organic acid hydrazide, diaminomaleonitriles or melamines or mixtures thereof. Also, it does not matter whether the curing agent has high polarity or not. For hardening of ethylene-glycidyl (meth)acrylate copolymer, a curing agent containing carboxyl group (including acid anhydride) in the molecule or rosin has to be used as

disclosed in Japanese Unexamined Patent Publication (Kokai) Nos. 9-137028 and 10-316955. This is because such a curing agent easily compatibilize ethylene-glycidyl (meth)acrylate copolymer and hardens glycidyl group in the ethylene-glycidyl (meth)acrylate copolymer, while a curing agent with high polarity cannot compatibilize ethylene-glycidyl (meth)acrylate copolymer, and cannot substantially react with it.

The curing agent may be used in combination with a curing accelerator. In particular, a curing accelerator comprising phenol containing compound, imidazole derivative, or tertiary amine can be advantageously used for reaction of a curing agent containing carboxyl group with epoxy.

A filler containing, for example, calcium carbonate or silica or mixture thereof, is added to the heat-curable resin composition. A filler can be used to decrease the coefficient of linear expansion of the hardened product. As a result, such a hardened product has reduced coefficient of linear expansion, especially in the temperature variation at low temperature, and amount of shrinkage at low temperature is thereby decreased so that paint film formed by aforementioned coating car paint thereon is hardly subjected to stress. Thus, crack is hardly produced at low temperature in the paint film formed in this manner.

When a filler is added in this manner, in general, the heat-curable resin composition may exhibit undesirable fluidity during heating-melting process. Therefore, it is preferable to include a plasticizer in the heat-curable resin composition of the present invention. By containing a plasticizer, the heat-curable resin composition of the present invention can retain desired fluidity, since the plasticizer generally has low viscosity and can contribute to the improvement of the fluidity of the composition.

Plasticizers that can be included in the heat-curable resin composition of the present invention include, for example, plasticizer containing phthalic acid esters such as phthalic acid di-2-ethylhexyl or phthalic acid diisononyl, adipic acid esters, epoxidized fatty acid esters, epoxidized soybean, epoxidized linseed oil, liquid terpene resin, liquid terpene phenol copolymer or liquid terpene styrene copolymer, azelaic acid esters, sebacic acid esters, epoxyhexaphthalic acid esters or mixtures thereof. Such plasticizers can give flexibility to the hardened product of the heat-curable resin composition. The glass transition temperature can be lowered, and elastic modulus at low temperature can be thereby decreased at temperature of -20 to -40 °C. As a result, the hardened product can

produce large elongation at low temperature, and dynamic durability such as vibrational durability can be thereby improved.

The sealing material which is formed by shaping such a heat-curable resin composition into a definite shape such as a sheet, tape, rope, or strap, is mounted on a discontinuous portion such as a joint. Then, the sealing material is heated and becomes capable of melting-flowing so as to seal the discontinuous portion. That is, it is heated to soften while it covers the discontinuous portion, and comes into close contact with the surface of the discontinuous portion and thereby expels the trapped air outwards. Then, the sealing material is hardened (that is, cross-linking through covalent bond is formed) by heating. It is prevented from being fluidized again by subsequent cooling and reheating. In automobile industry, such a discontinuous portion is found, for example, in a roof ditch, to which the sealing material of the present invention is applied. Such a sealing material is constrained not only by the bottom surface but also by the side wall of the roof ditch. The roof ditch may exert stress upon the sealing material from the side walls due to deviation and deflection of the panel constituting it. However, owing to the elasticity of the heat-curable resin composition, the sealing material can flexibly follow the deformation and cracks are hardly produced even when subjected to the stress from the side walls at relatively low temperature of about -30 °C. Therefore, ingress of dust, moisture, or other undesirable component can be prevented.

In automobile industry, after the sealing material in the roof ditch is heated to melt and flow, while a paint film is formed on the sealing material in the subsequent painting process, the sealing material is hardened in heating process. The paint film is constrained by the side walls of the roof ditch in the same manner as the sealing material, and in addition, it is also constrained by the sealing material. As a result, an interfacial stress is generally produced between the paint film and the sealing material. Usually, this interfacial stress is often observed at low temperature, since typical sealing material is subjected to shrinkage at low temperature. Based on the assumption that the interfacial stress (P) is generally relaxed at temperature equal to or higher than the glass transition temperature (T_g) of the sealing material, the interfacial stress (P) is expressed by following equation at temperature (T) equal to or lower than the glass transition temperature of the sealing material:

$$P = \Delta T \cdot E \cdot \Delta \alpha$$

where, $\Delta T : T - T_g$, E: elastic modulus of the sealing material, and $\Delta\alpha$: difference of the coefficient of linear expansion between the paint film and the sealing material.

In the case of the sealing material of the present invention, elastic modulus is low, and difference of coefficients of linear expansion is small, as has been described above.
5 As a result, at low temperature of -40 to -20 °C which is equal to or lower than the glass transition temperature (specifically, -30 to -10 °C) of the sealing material of the present invention, stress is reduced and production of crack in the paint film can be prevented.

Also, as has been described above, the sealing material of the present invention has reduced moisture before and after hardening. Therefore, even if painting is performed
10 after the sealing material has been left under high temperature and high pressure for several days before painting process, the problem arising from foaming and expansion of moisture, the problem that the sealing material does not adhere closely to the discontinuous portion and therefore leads to separation between layers or rising-up of layers, can be prevented, and hence, ingress of dust, moisture, and other undesirable
15 component can be avoided. Such a sealing material adheres satisfactorily to the paint film, and can give desirable appearance to the paint film.

Further, the heat-curable resin composition may include a crystallizing agent consisting of fine particulate metal, inorganic particles, crystalline polymer and organic pigment. When a crystalline resin such as polyester is contained in the heat-curable resin
20 composition, such a crystallizing agent can promote crystallization of the crystalline resin, and as a result, can prevent secular change of the performance of the heat-curable resin composition and its shaped body, the sealing material.

The heat-curable resin composition may include a refining agent for improving the close contact with a paint film provided on it as long as the effect of the present invention
25 is not impaired. Such a refining agent is a tackifier such as terpene resin or olefin copolymer in which components of relatively high polarity are copolymerized.

The sealing material of the present invention can be manufactured in various shaping methods using the above-described heat-curable resin composition. Obtained shaped body may be used as it is, or may be cut into a predetermined size, or may be
30 wound in the form of a roll.

Examples

The present invention will be described below with reference to examples thereof. It is to be understood that the present invention is by no means limited by these examples.

Example 1

5 Preparation of the sealing material:

Following components were mixed uniformly in the described amount to prepare a heat-curable resin composition.

Thermoplastic polyamide resin (trade name: "Macromelt 6238", manufactured by Henkel Co.): 50 parts by weight

10 Epoxy resin (trade name: "Epikote 1001", manufactured by Yuka Shell Epoxy Co.): 40 parts by weight

Dicyandiamide (curing agent, trade name: "EH 3636 AS", manufactured by Asahi Denka Co.): 7 parts by weight

15 Triazine derivative (curing accelerator, trade name: "2MZA", manufactured by Shikoku Co.): 3 parts by weight

These components were charged into a biaxial extruder and kneaded until uniform mixture was obtained. Then, obtained resin composition was extruded from the extruder, and was applied to a silicone treated surface of a PET film of 100 μm in thickness using a hot knife coater (Comma coater type) and dried. A resin sheet of 4 mm in thickness was
20 obtained.

Obtained resin sheet was placed on a thin-plate shaping die manufactured with 2-liquid silicone resin which has a continuous group of saw-tooth shape protrusions with cross section of rectangular equilateral triangle (base 1 mm, equilateral sides 0.71 mm) at a pitch of 1 mm, and the protrusion group of the shaping mold was transferred to the resin sheet under a heat press at 120 °C. By separating the resin sheet from the shaping mold, a
25 sealing material having narrow grooves of V-shaped cross section continuously formed on one surface was obtained.

Next, in order to use obtained sealing material in simulation test of a roof ditch of a car, the sealing material was cut to strips of width 7 mm \times length 150 mm to match the U-
30 shaped groove of the roof ditch. The strip-shaped sealing material had the form as described before with reference to Fig. 2, and V-shaped communicating grooves were arranged continuously in the direction perpendicular to the longitudinal direction.

Referring to Figs. 7 and 8, the size of each communicating groove was: angle $\theta_1 = 90$ degrees, pitch $P = 1$ mm, angle $\theta_2 = 90$ degrees, and a side 15 a of the groove = 0.71 mm.

Example 2

5 The procedure as described in the Example 1 above was repeated with the size of the communicating groove of the sealing material changed in this example as follows: angle $\theta_1 = 90$ degrees, pitch $P = 2$ mm, angle $\theta_2 = 90$ degrees, and a side 15 a of the groove = 1.4 mm.

10 Example 3

 The procedure as described in the Example 1 above was repeated with the size of the communicating groove of the sealing material changed in this example as follows: angle $\theta_1 = 60$ degrees, pitch $P = 1$ mm, angle $\theta_2 = 90$ degrees, and a side 15 a of the groove = 0.71 mm. Thus, in the sealing material in this Example, pattern of the
15 communicating groove was changed as shown in Fig. 9A.

Example 4

 The procedure as described in the Example 1 above was repeated with the size of the communicating groove of the sealing material changed in this example as follows:
20 angle $\theta_1 = 30$ degrees, pitch $P = 1$ mm, angle $\theta_2 = 90$ degrees, and a side 15 a of the groove = 0.71 mm. Thus, in the sealing material in this Example, pattern of the communicating groove was changed as shown in Fig. 9B.

Example 5

25 The procedure as described in the Example 1 above was repeated with the size of the communicating groove of the sealing material changed in this example as follows: angle $\theta_1 = 90$ degrees, pitch $P = 2$ mm, angle $\theta_2 = 120$ degrees, and a side 15 a of the groove = 1.2 mm.

30 Example 6

 The procedure as described in the Example 1 above was repeated with the size of the communicating groove of the sealing material changed in this example as follows:

angle $\theta_1 = 90$ degrees, pitch $P = 1$ mm, angle $\theta_2 = 120$ degrees, and a side 15 a of the groove = 0.6 mm.

Example 7

5 The procedure as described in the Example 1 above was repeated with the size of the communicating groove of the sealing material changed in this example as follows: angle $\theta_1 = 90$ degrees, pitch $P = 1$ mm, angle $\theta_2 = 60$ degrees, and a side 15 a of the groove = 1 mm.

10 Example 8

 The procedure as described in the Example 1 above was repeated, except that, in this example, when obtained sealing material was made available to simulation test of a roof ditch of car, the condition of precure process to be described below in the section on evaluation test, was changed from 120 °C/15 minutes (product temperature) to 140 °C/30
15 minutes (product temperature).

Comparative example 1

 The procedure as described in the Example 1 above was repeated, except that, in this example, for comparison, V-shaped communicating groove was omitted from the
20 surface of the sealing material. Thus, in this example, the obtained resin sheet was heat-shaped on a flat plate mold to manufacture a sealing material with flat surface.

Comparative example 2

 The procedure as described in the Example 1 above was repeated, except that, in
25 this example, for comparison, the communicating grooves were formed in parallel to the longitudinal direction of the sealing material. Thus, the sealing material in this example has communication grooves of pattern as shown in Fig. 10, with the size of each communicating groove 15 as follows: angle $\theta_1 = 0$ degrees, pitch $P = 1$ mm, angle $\theta_2 = 90$ degrees, and a side 15 a of the groove = 0.71 mm.

30

Comparative example 3

The procedure as described in the Comparative example 2 above was repeated, except that, in this example, the size of the communicating groove of the sealing material was changed as follows: angle $\theta_1 = 0$ degrees, pitch $P = 1$ mm, angle $\theta_2 = 120$ degrees, and a side 15 a of the groove $= 0.6$ mm.

Comparative example 4

The procedure as described in the Comparative example 2 above was repeated, except that, in this example, when obtained sealing material was made available to simulation test of a roof ditch of car, the condition of precure process to be described below in the section on evaluation test, was changed from $120^\circ\text{C}/15$ minutes (product temperature) to $140^\circ\text{C}/30$ minutes (product temperature).

Simulation test

The sealing material fabricated in above-described Examples and Comparative examples were used to conduct the simulation test of a car roof ditch in the following steps. This simulation test was conducted for evaluating whether or not the sealing material can provide a high quality seal without giving rise to trapping of air bubbles when the sealing material is actually applied for sealing a roof ditch.

Preparation of test specimens

In order to simulate a car roof ditch, test specimens having a shape similar to that shown in Fig. 3, were prepared using panels of cold rolled steel plate 0.8 mm in thickness. After two panels were folded on a crank as shown, the surfaces of end portion of respective panels were superimposed and spot-welded to each other, and finally, entire panel was subjected to cation electrodeposition coating of automobile grade. Size of the obtained test specimen having U-shaped ditch was as follows: length $L = 400$ mm, width of the ditch $w = 9$ mm, depth $d = 7$ mm, height of step A $h = 0.8$ mm, width $a = 3$ mm.

Simulation test

The sealing material was mounted on the ditch portion of the fabricated test specimen such that the communicating grooves of the sealing material covered the step of

the test specimen as shown in Fig. 3. Then, the test specimen was placed into a thermostatic oven, and was allowed to remain at 120 °C (product temperature) for 15 minutes. This was intended to simulate a process called precure process usually included in an automobile painting line for preliminary drying of the sealing material. In this
5 precure process, solid sealing material was made to melt and flow by heating, and filled the ditch so as to cover longitudinal wall on both sides.

Thereafter, following heating processes were successively performed to simulate the painting process usually performed in an automobile painting line. Painting was not actually performed in these heating processes because, if paint film was present on the
10 surface of a seal formed by hardening of the sealing material, it was difficult to measure the diameter or the like of the trapped air bubbles on the seal surface.

First heating process:

The test specimen was placed into a thermostatic oven and was heated at 140 °C
15 for 30 minutes (product temperature) to harden the sealing material as a simulation of an intercoating process which is typically performed by electrostatic coating of an acrylic solid paint.

Second heating process:

20 The test specimen was placed into a thermostatic oven and was heated at 140 °C for 30 minutes (product temperature) to harden the sealing material as a simulation of a topcoating process which is typically performed by electrostatic coating of an acrylic solid paint.

After above-described heating processes were completed, the test specimen was
25 left for 24 hours at room temperature and the surface of the obtained seal was inspected visually and observed air bubbles was counted. Measured number of air bubbles for each test specimen (average of 5 measurements) is shown in Table 1 below.

Then, each of air bubbles in the seal was observed with a microscope (manufactured by Keyence Co., Model VH-6300) at magnification of $\times 20$, and diameter of
30 respective air bubbles was measured on the monitor. Diameter of air bubble (average of 5 measurements) was substituted into the following formula (formula of volume of a sphere).

$$\text{Volume of a sphere } V = (4/3) \times \pi \times (D/2)^3$$

For each test specimen, the volume V of a sphere was summed up for air bubbles in the specimen, and by averaging, air bubble equivalent volume per specimen (volume of air bubbles surmised to be trapped in the seal) was calculated. Air bubble equivalent volume thus obtained is shown in Table 1 below.

Table 1

| Example No. | Number of Trapped Air Bubbles (pcs) | Air Bubble Equivalent Volume (mm ³) | Evaluation |
|-----------------------|-------------------------------------|---|------------|
| Example 1 | 1 | 0.04 | Ⓔ |
| Example 2 | 1 | 0.05 | Ⓔ |
| Example 3 | 2 | 0.10 | Ⓔ |
| Example 4 | 2 | 0.04 | Ⓔ |
| Example 5 | 1.5 | 0.14 | Ⓔ |
| Example 6 | 2 | 0.19 | Ⓔ |
| Example 7 | 2 | 0.21 | Ⓔ |
| Example 8 | 1 | 0.03 | Ⓔ |
| Comparative example 1 | 4.2 | 3.5 | Ⓢ |
| Comparative example 2 | 5.5 | 1.6 | Ⓢ |
| Comparative example 3 | 5 | 1 | Ⓢ |
| Comparative example 4 | 10 | 1.7 | Ⓢ |

As can be understood from the evaluation in Table 1 above, in Examples 1 to 8, during melting-hardening of the sealing material, air bubbles trapped under the sealing material were able to escape through the rugged communicating groove so that number of air bubble trapping points per specimen was small and, even if there were trapped air bubbles, its volume was quite small and was thus within an acceptable range. Therefore, the sealing material in these Examples could be judged as acceptable (Ⓔ).

On the contrary, when the bonding surface (seal surface) of the sealing material was untreated and flat as in Comparative example 1, number of air bubble trapping points

per specimen was large and air bubble equivalent volume was also large. When communicating grooves were provided in parallel to the longitudinal direction of the sealing material as in Comparative examples 2 to 4, air bubbles were accumulated and led to a large defect. Therefore, the sealing material in these Comparative examples could only be judged as unacceptable (③).

As has been described in detail in the foregoing, in accordance with the present invention, there is provided a sealing material for vehicle, which can be handled easily, does not produce harmful gases to environment, is capable of preventing air bubbles from being trapped even when the joint portion is a surface of irregular shape, and therefore does not give rise to poor appearance or defects in paint film. The sealing material of the present invention can exhibit its operative effect fully especially when it is applied for sealing a discontinuous joint portion of a vehicle, for example, a roof ditch.

In the Claims:

1. A sealing material that can be used for sealing a discontinuous joint portion, said sealing material comprising a shaped body of a heat-curable resin composition, which is capable of melting-hardening and which has sufficient width and length to substantially cover said joint portion, characterized by said shaped body being provided with a plurality of communicating grooves, and each of said communicating grooves has a starting end at one side of said shaped body and a terminating end at the other opposing side of said shaped body.
2. The sealing material according to claim 1, wherein said grooves are aligned in a predetermined direction and arranged in parallel to each other on the surface to be brought in contact with said joint portion.
3. The sealing material according to claim 1 or 2, wherein said joint portion is a lap joint of longer sides of longitudinal metal plates.
4. The sealing material according to any one of claims 1 to 3, wherein said joint portion defines a bottom surface of a groove of a longitudinal grooved plate.
5. The sealing material according to claim 4, wherein said grooved plate is a roof ditch of an automobile.
6. The sealing material according to any one of claims 1 to 5, wherein said communicating groove has a cross-sectional shape selected from the group consisting of rectangle, semicircle, V-shape, U-shape, and trapezoid.
7. The sealing material according to any one of claims 1 to 6, wherein said heat-curable resin composition comprises:
- a heat-curable epoxy-containing material;
 - a thermoplastic polyamide component a having softening point lower than the curing temperature of said epoxy-containing material; and

a curing agent for said epoxy-containing material.

8. The sealing material according to any one of claims 1 to 6, wherein said heat-curable resin composition comprises:

5 an epoxy-containing material comprising a hygroscopic epoxidized thermoplastic resin;

a curing agent for said epoxy-containing material; and

a filler.

10 9. The sealing material according to claim 8, wherein said heat-curable resin composition further comprises a plasticizer.

15 10. The sealing material according to claim 8 or 9, wherein said hygroscopic epoxidized thermoplastic resin is at least one of an epoxidized ethylene thermoplastic resin and an epoxidized styrene thermoplastic resin.

1/5

FIG. 1A

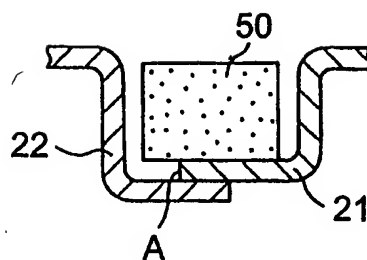


FIG. 1B

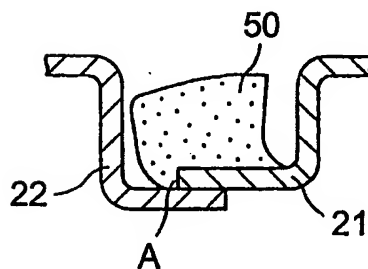


FIG. 1C

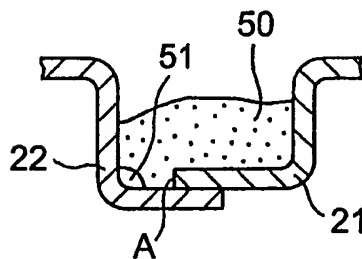


FIG. 1D

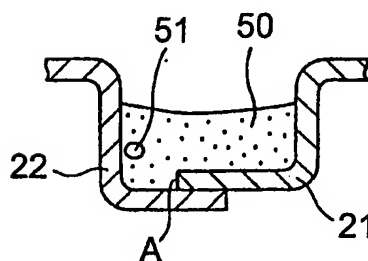


FIG. 1E

